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# Acid-Catalyzed Isomerization of 1-Acyl- and 1-Thioacylaziridines. III. 2-Phenylaziridine Derivatives


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Acid-catalyzed isomerizations of (*R*)-1-(*N*-phenylcarbamyl)- (**1a**) and (*R*)-1-(*N*-phenylthiocarbamyl)-2-phenylaziridine (**1b**) were investigated to see the effect of the ring phenyl group on the orientation of the ring opening and the stereochemistry at the asymmetric carbon atom. Throughout the isomerizations of **1a** and **1b**, exclusive N–CHPh bond cleavage was observed. With protonic acids, **1a** gave partially (40%) racemized 2-anilino-5-phenyl-2-oxazoline (**2a**), and with boron trifluoride etherate, it gave highly (95%) racemized **2a**. The thiourea **1b** gave 2-anilino-5-phenyl-2-thiazoline (**2b**) in good yields with protonic acids and in a poor yield with boron trifluoride etherate.

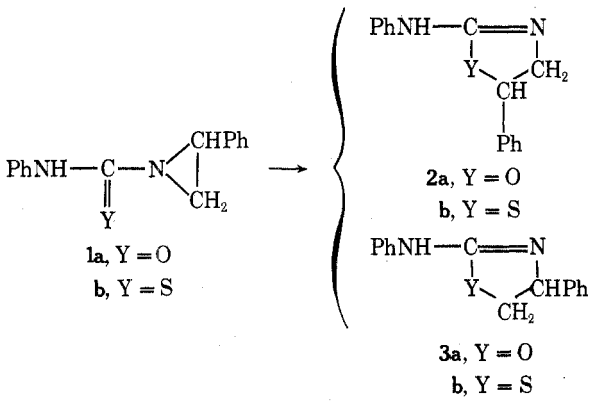

A variety of acid-catalyzed isomerizations of 1-acyl- and 1-thioacylaziridines to 2-oxazolines[1] or thiazolines[1a,f,2] have been observed, and mechanistic studies of these reactions have been done by several workers. Heine and coworkers[1e] found that 1-aroyl-2,2-dimethyl- or 1-aroyl-2-phenylaziridine isomerized in cold sulfuric acid to 2-aryl-5,5-dimethyl- or 2-aryl-5-phenyl-2-oxazoline, respectively. Deutsch and Fanta[2a] reported that the isomerization of 1-(*N*-phenylthiocarbamyl)-2,2-dimethylaziridine with hot concentrated hydrochloric acid gave 2-anilino-5,5-dimethyl-2-thiazoline. These reactions were considered to proceed via a carbonium ion from the orientation of the ring opening (so-called "abnormal" cleavage).

Our previous study[3] was planned to see if an "abnormal" cleavage would always give rise to a carbonium ion in the acid-catalyzed isomerizations of 1-acyl- or 1-thioacylaziridines, and further to correlate the orientation with the mechanism of the ring opening. (*S*)-1-(*N*-Phenylcarbamyl)-2-methylaziridine (**1a'**) isomerized to 2-anilino-5-methyl-2-oxazoline (**2a'**) with 100% retention of configuration either with protonic acids or with boron trifluoride etherate in refluxing benzene. This means that the conversion of (*S*)-**1a'** to (*S*)-**2a'** ("abnormal" cleavage) has not proceeded via a free carbonium ion. As for the orientation of the ring opening, very puzzling results were obtained and no correlation could be found between the orientation and the mechanism of the ring opening deduced from the stereochemistry: **1a'** gave **2a'** as the major product (80–90%), while 1-(*N*-phenylthiocarbamyl)-2-methylaziridine (**1b'**) gave nearly equal amount of 2-anilino-5-methyl-2-thiazoline (**2b'**) and 2-anilino-4-methyl-2-thiazoline (**3b'**). Optically active **1b'** gave racemic **2b'** in some cases in contrast with **1a'**.

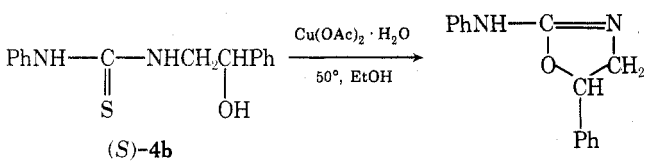
Replacing the 2-methyl group with a phenyl group seemed interesting from the following two points: (1) whether in this case, also, the "abnormal" cleavage would give the oxazoline with retention of configuration, and (2) what would be the orientation of the ring opening especially with the thiourea derivative. Heine and Kaplan[1e] reported that the thermal isomerization of *cis*-1-(*p*-nitrobenzoyl)-2,3-diphenylaziridine gave *cis*-2-(*p*-nitrophenyl)-4,5-diphenyl-2-oxazoline, and the corresponding trans compound gave the trans oxazoline. So far, no stereochemical investigation of the acid-catalyzed isomerization of 2-aryl- or 2,3-diarylaziridine derivatives has been reported.

The present study deals with the isomerization of (*R*)-1-(*N*-phenylcarbamyl)- (**1a**) and (*R*)-1-(*N*-phenylthiocarbamyl)-2-phenylaziridine (**1b**). (*R*)-2-Phenylaziridine was prepared from (*R*)-2-amino-2-phenylethyl alcohol by the Wenker method. Reaction of (*R*)-2-phenylaziridine with phenyl isocyanate gave **1a**. (*R*)-1-(*N*-Phenylthiocarbamyl)-2-phenylaziridine (**1b**) which was prepared from the same aziridine and phenyl isothiocyanate could not be recrystallized owing to the tendency to polymerize in solution.

Authentic samples of the isomerization products (**2a, 2b, 3a,** and **3b**) were prepared. Optically pure samples of (*R*)-2-anilino-4-phenyl-2-oxazoline (**3a**) and (*R*)-2-anilino-4-phenyl-2-thiazoline (**3b**) were prepared from (*R*)-1-(1'-phe-



nyl-2′-hydroxyethyl)-3-phenylurea and the corresponding thiourea by dehydration with polyphosphoric acid (PPA). However, dehydration of both (*S*)-1-(2′-hydroxy-2′-phenylethyl)-3-phenylurea (**4a**) and the thiourea derivative (**4b**) under the same conditions gave racemic **2a** and **2b.** It was previously[4] found that the reaction of 1-(3′-phenoxy-2′-hydroxypropyl)-3-phenylthiourea with cupric acetate in refluxing ethanol gave 2-anilino-5-phenoxymethyl-2-oxazoline in 73% yield. Treatment of **4b** under the same conditions led to extensive decomposition, but at 50°, we obtained an optically pure sample of (*S*)-**2a** from (*S*)-**4b** pre-



(*S*)-**4b** (*S*)-**2a**

$[\alpha]^{30}D$ +77° (0.2298 g/10 ml in dioxane)

pared from (*S*)-1-phenyl-2-aminoethanol and phenyl isothiocyanate. We have not succeeded in the preparation of optically pure sample of **2b** so far.

The isomerization of (*R*)-**1a** was tried with *p*-toluenesulfonic acid, picric acid, and boron trifluoride etherate in refluxing benzene. In all cases, the rearranged product was composed of 100% **2a,** and no trace of **3a** was found by the NMR analysis. The specific rotations of the products are shown in Table I. The reaction of (*R*)-**1b** with *p*-toluenesulfonic acid, picric acid, or boron trifluoride etherate was carried out in the same way, and gave 100% **2b** in every case, though in a very low yield with boron trifluoride etherate. Results are summarized in Table I.

The isomerization of **1a** to **2a** proceeded with 60% retention of configuration on the asymmetric carbon atom with protonic acids, and 5% with boron trifluoride etherate. The 60% retention with protonic acids suggests that the conjugate bases of the acids should have participated in the reaction. An ion-pair formation between the conjugate base of the acid and the forming carbonium ion might explain the partial retention of configuration since an addition–elimination process should lead to a complete retention of configuration. Under similar conditions, *p*-nitrobenzoic acid and **1a** gave an addition product which was found to be 1-[2′-(*p*-nitrobenzoyloxy)-2′-phenylethyl]-3-phenylurea (**5**). Comparison of the optical rotations of authentic (*S*)-**5** and the addition product showed that the addition reaction had taken place with complete inversion of configuration. An intramolecular ion pair seems less likely as an intermediate of the isomerization of **1a** to **2a** with protonic acids, since **1a** gave highly (95%) racemized **2a** with boron trifluoride etherate. The latter reaction must have proceeded via a free carbonium ion.

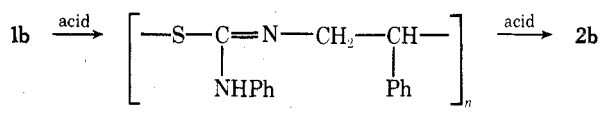
**Table I**
**Isomerization of 1a and 1b with Acids**

| | Acid | Yield of **2**, % | $[\alpha]D^a$ | % of retention[b] |
|---|---|---|---|---|
| (*R*)-**1a** | *p*-Toluenesulfonic | 86 | −47 | 61 |
| | Picric | 76 | −46 | 60 |
| | $BF_3 \cdot OEt_2$ | 69 | −4 | 5 |
| (*R*)-**1b** | *p*-Toluenesulfonic | 81 | +95 | |
| | Picric | 75 | +97 | |
| | $BF_3 \cdot OEt_2$ | 9 | +100 | |

[a] Measured in dioxane, at 28° in the case of **2a**, and 24° with **2b**. [b] Calculated from the equation $-100[\alpha]D/77$, where 77 is a value for the specific rotation of (*S*)-**2a**.

It is noted in the isomerization of **1b** that the specific rotations of **2b** are almost the same in three cases. Therefore, the optical purity of **2b** from the isomerization of (*R*)-**1b** is supposed to be fairly high. The ir spectra (in KBr pellets) of **2b** thus obtained are different from that of (*R,S*)-**2b,** and a similar difference is also found between the spectra of (*S*)- and (*R,S*)-**2a.** Participation of the conjugate bases of protonic acids is not likely, since boron trifluoride etherate gave **2b** of similar specific rotation. Three ways may be conceivable which would explain the results: (1) an intramolecular ion-pair formation, (2) participation of another molecule of **1b** as a nucleophile, and (3) intervention of a polymer of **1b** with iminothioether structures. There has been no fact which would favor or disfavor any one of the three. However, we would like to think of 1 only after the other possibilities have been crossed out, since the structure of such an ion pair is highly strained.

Previous papers[5,6] have shown that 1-thioacylaziridines polymerize to give polymers with iminothioether structures, and such polymers give thiazolines on heating with acids. A low molecular polymer of (*R*)-**1b** ($\eta_{sp/c}$ = 0.1) obtained by allowing a solution of **1b** to stand with a small amount of boron trifluoride etherate gave **2b** in 55% yield



on heating with *p*-toluenesulfonic acid in refluxing benzene, and the specific rotation of **2b** thus obtained was +101°. When the reaction of **1b** with *p*-toluenesulfonic acid was stopped in 5 min, **1b** was not recovered but **2b** and some polymeric material were obtained from the reaction mixture. These facts coupled with the results reported previously[5,6] suggest that 3 could be possible.

As a summary, the effect of the ring phenyl group definitely appeared in the orientation of the ring opening: throughout the isomerizations of **1a** and **1b,** exclusive N–CHPh bond cleavage was observed. This is in marked contrast to the case with **1a′** and **1b′,** where always N–CHMe and N–$CH_2$ bond cleavages were taking place at the same time in varying ratios depending upon the materials and the reaction conditions. Stereochemically, **1a** gave **2a** with 60% retention of configuration with protonic acids, while **1a′** isomerized to **2a′** with complete retention under the same conditions. Moreover, in contrast to the fact that (*S*)-**1a′** gave optically pure (*S*)-**2a′** with boron trifluoride or boron trifluoride etherate under varying conditions (presumably by an SNi mechanism), (*R*)-**1a** gave almost racemic **2a** on heating with boron trifluoride etherate in refluxing benzene. These facts may be explained by the greater ion-stabilizing and the steric effects of the phenyl group in **1a** than those of the methyl in **1a′,** which would tend to favor SN1 reaction rather than SN2 or SNi.

## Experimental Section

All melting and boiling points are uncorrected. Ir spectra were recorded on a Shimazu Model IR-27G instrument. NMR spectra were obtained on a Hitachi Model R-20B spectrometer. Optical rotations were determined on a Jasco Model DIP-SL automatic polarimeter.

**Preparation of (*R*)-2-Phenylaziridine.** Reduction of (*R*)-2-phenylglycine with $LiAlH_4$ in THF gave (*R*)-2-amino-2-phenylethanol, mp 76.6–77.8° (lit.[7] 78–79°), $[\alpha]^{23}D$ −27.6° (0.9928 g/10 ml, EtOH) [lit.[7] $[\alpha]^{15}D$ −27.5 ± 0.5° (0.993 g/10 ml, EtOH)].

The cyclization of the amino alcohol to (*R*)-2-phenylaziridine was carried out according to the Wenker method via the hydrogen sulfate. When an aqueous solution of the sulfuric acid salt of the amino alcohol was evaporated under reduced pressure, the salt sometimes crystallized out, and this crystallization prevented smooth dehydration of the salt to the ester. Therefore, the bath temperature was quickly raised to 150° before the crystallization began. Starting from 23 g of the amino alcohol, 17 g (84%) of (*R*)-2-phenylaziridine was obtained, bp 73° (4 mm).

That racemization was not taking place during the synthesis was shown by the fact that the specific rotation was practically the same with samples from two separate preparations: $[\alpha]^{26}D$ −43.4° (1.0062 g/10 ml, EtOH) and −42.7° (1.0123 g/10 ml, EtOH).

**(*R*)-1-(*N*-Phenylcarbamyl)-2-phenylaziridine [(*R*)-1a]** was obtained by the reaction of (*R*)-2-phenylaziridine with phenyl isocyanate in ether, and recrystallized from benzene and *n*-hexane: mp 114.0–116.0°; $\nu$ (KBr) 1655 $cm^{-1}$ (C=O); $\delta$ ($CDCl_3$) 2.13 ($\delta_A$), 2.74 ($\delta_M$), 3.35 ($\delta_X$) (AMX, $J_{AM}$ = 0.7, $J_{AX}$ = 3.9, $J_{MX}$ = 6.8 Hz, 3, ring H), 7.20 (m, 10, aromatic H), 7.67 (s, 1, NH); $[\alpha]^{26}D$ −262° (0.5078 g/10 ml, dioxane).

Anal. Calcd for $C_{15}H_{14}N_2O$: C, 75.60; H, 5.92; N, 11.76. Found: C, 75.78; H, 5.93; N, 11.82.

**(*R*)-1-(*N*-Phenylthiocarbamyl)-2-phenylaziridine [(*R*)-1b].** To a solution of 1.3 g (9.6 mmol) of phenyl isothiocyanate in 20 ml of petroleum ether (bp 35–80°) was added a solution of 1.3 g (10.9 mmol) of (*R*)-2-phenylaziridine in 12 ml of ether dropwise at −10°. After addition, the reaction mixture was stirred for 1 hr at −10°. Meanwhile crystals separated out. They were collected on a filter, washed with cold ether–petroleum ether mixture, and dried at 0° to give 2 g of crude (*R*)-1b. All attempts to recrystallize the crude product failed. Crude (*R*)-1b melted at about 80°; $\delta$ ($CDCl_3$) (at −10°) 2.54 ($\delta_A$), 2.78 ($\delta_M$), 3.39 ($\delta_X$) (AMX, $J_{AM}$ = 0, $J_{AX}$ = 5.0, $J_{MX}$ = 3.2 Hz, 3, ring H), 6.8–7.4 (m, 10, aromatic H), 9.31 (s, 1, NH). Deterioration of the sample was noted while the NMR was taken, and no crystalline material was recovered after evaporation of $CDCl_3$ from the solution. Optical rotation was measured with the crude samples right after preparation: $[\alpha]^{24}D$ −177° (0.3442 g/10 ml, dioxane) and −174° (0.0604 g/10 ml, dioxane).

Anal. Calcd for $C_{15}H_{14}N_2S$: C, 70.85; H, 5.55; N, 11.02. Found: C, 70.73; H, 5.58; N, 10.83.

**Preparation of (*R*)-2-anilino-4-phenyl-2-oxazoline [(*R*)-3a] and (*R*)-2-anilino-4-phenyl-2-thiazoline [(*R*)-3b].** From (*R*)-2-amino-2-phenylethanol and phenyl isocyanate, (*R*)-1-(1′-phenyl-2′-hydroxyethyl)-3-phenylurea was obtained, mp 164.0–165.5°, $\nu$ (KBr) 1637 $cm^{-1}$ (C=O).

A mixture of 7 g of PPA and 7 ml of dioxane was kept at 80°. To this was added 1.0 g (3.9 mmol) of above-obtained urea, and the mixture was stirred for 8 hr at 80°. Then the reaction mixture was poured into ice-cold 2 *N* NaOH. Extraction of the basified aqueous layer with benzene and evaporation of the solvent gave 0.8 g of crude (*R*)-3a. Recrystallization from a benzene–petroleum ether mixture gave 0.7 g (75%) of an analytically pure sample: mp 119.0–120.5°; $\nu$ (KBr) 1695–1707 $cm^{-1}$ (C=N); $\delta$ ($CDCl_3$) 4.05 ($\delta_X$), 4.58 ($\delta_A$), 5.00 ($\delta_B$) (ABX, $J_{AB}$ = 8.7, $J_{AX}$ = 7.7, $J_{BX}$ = 7.4 Hz, 3, ring H), 7.0–7.3 (m, 10, aromatic H), 8.51 (s, 1, NH); $[\alpha]^{23}D$ −164° (0.4960 g/10 ml, dioxane).

Anal. Calcd for $C_{15}H_{14}N_2O$: C, 75.60; H, 5.92; N, 11.76. Found: C, 75.67; H, 5.75; N, 11.83.

In a similar manner, (*R*)-3b was prepared from (*R*)-1-(1′-phenyl-2′-hydroxyethyl)-3-phenylthiourea (mp 96–100°). Crude product was recrystallized from benzene and petroleum ether to give an analytical sample: mp 132.7–135.0°; $\nu$ (KBr) 1639 $cm^{-1}$ (C=N); $\delta$ ($CDCl_3$) 3.07 ($\delta_B$), 3.39 ($\delta_A$), 4.88 ($\delta_X$) (ABX, $J_{AB}$ = 10.5, $J_{AX}$ = 6.8, $J_{BX}$ = 8.4 Hz, 3, ring H), 6.9–7.3 (m, 10, aromatic H), 8.23 (s, 1, NH); $[\alpha]^{24}D$ −224° (0.5080 g/10 ml, dioxane).

Anal. Calcd for $C_{15}H_{14}N_2S$: C, 70.85; H, 5.55; N, 11.02. Found: C, 70.90; H, 5.55; N, 11.11.

**2-Anilino-5-phenyl-2-oxazoline (2a) and 2-Anilino-5-phenyl-2-thiazoline (2b).** 1-Phenyl-2-aminoethanol was prepared by the $LiAlH_4$ reduction of mandelic amide in THF according to the literature[8], bp 107–114° (3 mm) [lit.[8] bp 116–117° (2 mm)].

Reaction of phenyl isocyanate with the amino alcohol gave 1-(2′-hydroxy-2′-phenylethyl)-3-phenylurea (**4a**), mp 184.0–185.0°, $\nu$ (KBr) 1633 $cm^{-1}$ (C=O). Dehydration of **4a** with PPA and the subsequent treatment as mentioned in the preparation of **3a** gave **2a** in a quantitative yield. Recrystallization from benzene and petroleum ether gave a pure sample: mp 124.0–125.0°; $\nu$ (KBr) 1642, 1665 (C=N), 3210, 3260 $cm^{-1}$ (NH); $\delta$ ($CDCl_3$) 3.73 ($\delta_B$), 4.17 ($\delta_A$), 5.50 ($\delta_X$) (ABX, $J_{AB}$ = 11.6, $J_{AX}$ = 8.9, $J_{BX}$ = 7.7 Hz, 3, ring H), around 7.3 (m, 10, aromatic H), 8.10 (s, 1, NH).

Anal. Calcd for $C_{15}H_{14}N_2O$: C, 75.60; H, 5.92; N, 11.76. Found: C, 75.35; H, 5.91; N, 11.74.

Similarly, 1-(2′-hydroxy-2′-phenylethyl)-3-phenylthiourea (**4b**, mp 127–129°) was prepared from the same amino alcohol and phenyl isothiocyanate, and dehydrated to give **2b**. Recrystallization from benzene and petroleum ether gave a sample melting at 113–116°; $\nu$ (KBr) 1625 (C=N), 3200, 3250 $cm^{-1}$ (NH); $\delta$ ($CDCl_3$) 3.77 ($\delta_B$), 3.99 ($\delta_A$), 4.83 ($\delta_X$) (ABX, $J_{AB}$ = 11.2, $J_{AX}$ = 6.9, $J_{BX}$ = 8.0 Hz, 3, ring H), 7.0–7.4 (m, 10, aromatic H), 7.97 (s, 1, NH).

Anal. Calcd for $C_{15}H_{14}N_2S$: C, 70.85, H, 5.55; N, 11.02. Found: C, 70.62; H, 5.48; N, 11.01.

**Preparation of (*S*)-2-Anilino-5-phenyl-2-oxazoline [(*S*)-2a].** (*S*)-1-Phenyl-2-aminoethanol was prepared in the same way as mentioned in the preparation of (*R,S*)-amino alcohol starting from (*S*)-mandelic acid. Crude amino alcohol was recrystallized from ether and petroleum ether, mp 61–63° (lit.[8] mp 61–62°), $[\alpha]^{23}D$ +44.8° (0.2088 g/10 ml, EtOH) {lit.[8] $[\alpha]^{18}D$ +44.6 ± 2.2° (0.206 g/10 ml, EtOH)}.

Reaction of the amino alcohol with phenyl isocyanate gave (*S*)-**4a** melting at 199.0–200.7°, $\nu$ (KBr) 1631 $cm^{-1}$ (C=O).

Anal. Calcd for $C_{15}H_{16}N_2O_2$: C, 70.29; H, 6.29; N, 10.93. Found: C, 70.55; H, 6.37; N, 10.84.

Compound (*S*)-**4a** had no appreciable optical rotation. Dehydration of (*S*)-**4a** with PPA gave (*R,S*)-**2a**.

(*S*)-1-(2′-Hydroxy-2′-phenylethyl)-3-phenylthiourea [(*S*)-**4b**] was obtained by the reaction of the (*S*)-amino alcohol with phenyl isothiocyanate. Crude (*S*)-**4b** was recrystallized from benzene and petroleum ether to give a pure sample, mp 83–87°.

Anal. Calcd for $C_{15}H_{16}N_2OS$: C, 66.16; H, 5.92; N, 10.29. Found: C, 66.54; H, 5.99; N, 10.32.

A mixture of 680 mg (2.5 mmol) of (*S*)-**4b**, 500 mg (2.5 mmol) of $Cu(OAc)_2 \cdot H_2O$, and 20 ml of EtOH was stirred at 50–55° for 3 hr. After the black precipitate of CuS was removed by centrifuge, the ethanolic solution was evaporated by rotary. The residue was dissolved in benzene, and the benzene solution was extracted with 2 *N* HCl three times. The aqueous layer was cooled and basified with NaOH, and was extracted with benzene. Drying the benzene solution with $Na_2SO_4$ and evaporation by rotary left a brown residue. The residue was dissolved in $CHCl_3$, and the solution was quickly passed through a silicic acid column. Evaporation of the solvent and recrystallization of the residue from benzene and petroleum ether gave 105 mg (17%) of (*S*)-**2a**, mp 124.0–125.0°, $[\alpha]^{30}D$ +77° (0.2298 g/10 ml, dioxane). Another cyclization reaction gave a sample, $[\alpha]^{28}D$ +84° (0.1062 g/10 ml, dioxane). The ir of (*S*)-**2a** in a KBr pellet was much different from that of (*R,S*)-**2a**, especially in the C=N and NH regions: $\nu$ (KBr) 1649, 1687 (C=N), 3110, 3175 $cm^{-1}$ (NH). In $CHCl_3$, their ir spectra were completely identical: $\nu$ ($CHCl_3$) 1673 $cm^{-1}$ (C=N).

Anal. Calcd for $C_{15}H_{14}N_2O$: C, 75.60; H, 5.92; N, 11.76. Found: C, 75.75, 75.71; H, 5.95, 5.95; N, 11.48, 11.51.

Dehydration of (*S*)-**4b** with PPA gave (*R,S*)-**2b**.

**Isomerization Reaction of (*R*)-1a with *p*-Toluenesulfonic Acid.** A solution of 1.0 g (5.9 mmol) of *p*-TosOH in 10 ml of benzene was stirred in a 100-ml three-necked flask with an addition funnel, a reflux condenser, and a stirrer, and the solution was heated to reflux. To the solution was added a solution of 1.27 g (5.1 mmol) of (*R*)-1a in 10 ml of benzene dropwise in 5 min, and the mixture was refluxed for 1 hr with stirring. After cooling, the benzene solution was washed with 2 *N* NaOH and then with water, and dried with $Na_2SO_4$. Evaporation of the solvent by rotary left 1.1 g (87%) of white residue. The NMR spectrum of the residue was completely identical with that of **2a**, and no trace of **1a** or **3a** was detected.

The crude product was dissolved in 2 *N* $H_2SO_4$, and the acidic solution was cooled and basified with NaOH. Extraction of the aqueous suspension with benzene and concentration of the benzene solution gave white crystals. After drying, the optical rotation of the crystalline product was measured.

Other isomerization reactions were carried out and the products

were treated in much the same manner. In the case of the reaction of **1b** with $BF_3$·$OEt_2$, the crude reaction product was mostly polymeric, though it had peaks of **2b** in the NMR spectrum. Extraction of the crude product with 2 *N* $H_2SO_4$, treatment of the acidic solution with NaOH, and the subsequent extraction of the alkaline suspension with benzene gave crystalline **2b** in 9% yield on evaporation of the solvent. The ir spectrum (KBr pellet) of **2b** thus obtained was different from that of (*R,S*)-**2b** especially in the NH regions: $\nu$ (KBr) 3090 $cm^{-1}$ (NH). However, the C=N regions were almost the same: $\nu$ (KBr) 1624 $cm^{-1}$ (C=N).

**Reaction of 1a with *p*-Nitrobenzoic Acid.** A solution of 476 mg (2 mmol) of (*R*)-**1a** and 368 mg (2.2 mmol) of *p*-nitrobenzoic acid in 10 ml of benzene was refluxed for 8 hr. After cooling, crystals were collected on a filter and the filtrate was concentrated to give an additional crop. The crude product was dissolved in ethyl acetate, and the solution was washed with 1*N* NaOH and water and dried with $Na_2SO_4$. Evaporation of the solvent gave 90 mg (12%) of **5** melting at 175–180°, $[\alpha]^{22}D$ +12.4° (0.1770 g/10 ml, THF). Recrystallization of the crude product from $CHCl_3$–petroleum ether gave a sample: mp 181.0–183.0°; $\nu$ (KBr) 1631 (urea C=O), 1727 (ester C=O), 3350 $cm^{-1}$ (NH); $\delta$ (in a 1:1 mixture of $CDCl_3$–$Me_2SO$-$d_6$) 3.77 (dd, 2, $CH_2$), 6.10 (t, 1, CH), 6.27 (d, 1, NH), 6.7–7.7 (m, 10, aromatic H), 7.7 (s, 1, NH), 8.23 (s, 4, aromatic H).

Anal. Calcd for $C_{22}H_{19}N_3O_5$: C, 65.18; H, 4.72; N, 10.37. Found: C, 65.48; H, 4.74; N, 10.60.

When the addition product **5** (20 mg) was treated with a solution of KOH (30 mg) in aqueous ethanol (2 ml) at room temperature, (*S*)-**4a** was obtained, mp 199–201°. [As mentioned before, authentic (*S*)-**4a** melts at 199.0–200.7°, and (*R,S*)-**4a** at 184.0–185.0°.] The mixture melting point with authentic (*S*)-**4a** was 199–201°.

An authentic sample of (*S*)-**5** was prepared by refluxing a solution of (*S*)-**4a** (1 mmol), *p*-nitrobenzoyl chloride (2 mmol), and $Et_3N$ (2 mmol) in 10 ml of THF for 4 hr. Recrystallization of the crude product from $CHCl_3$–petroleum ether gave a sample, mp 182–183°, $[\alpha]^{22}D$ +11.9° (0.0505 g/10 ml, THF).

The above obtained addition product **5** was found to be identical with (*S*)-**5** in all respects.

**Polymerization of (*R*)-1b, and the Reaction of the Polymer with *p*-TosOH.** A solution of 635 mg (2.5 mmol) of (*R*)-**1b** and 4 mg of $BF_3$·$OEt_2$ in 10 ml of benzene was kept at 5° for 1 week. The solution was washed with 1 *N* NaOH and water and dried ($Na_2SO_4$). Evaporation of the solvent left a pale yellow residue. The residue was dissolved in a small amount of benzene, and the solution was poured into a large volume of ether to give white precipitate, which was filtered and dried. The polymer weighed 313 mg (50%), melted at about 145°, and had an absorption at 1610 $cm^{-1}$ (presumably C=N) in the ir (KBr pellet). The viscosity in benzene solution (*c* 1 g/100 ml) was determined at 30°.

Anal. Calcd for $(C_{15}H_{14}N_2S)_n$: C, 70.85; H, 5.55; N, 11.02; S, 12.58. Found: C, 70.99; H, 5.56; N, 10.83; S, 12.60.

The polymer (254 mg) and *p*-TosOH (189 mg) were dissolved in 5 ml of benzene, and the solution was refluxed for 2 hr. The solution was washed with 2 *N* NaOH and water, dried ($Na_2SO_4$), and evaporated to give 140 mg (55%) of crystalline **2b**, $[\alpha]^{22}D$ +101°.

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**Registry No.**—(*R*)-**1a**, 33815-64-4; (*R*)-**1b**, 56533-11-0; (*R*)-**1b** polymer, 56533-12-1; (*R,S*)-**2a**, 56533-13-2; (*S*)-**2a**, 56586-18-6; (*R,S*)-**2b**, 56533-14-3; (+)-**2b**, 56533-15-4; (*R*)-**3a**, 56533-16-5; (*R*)-**3b**, 56533-17-6; (*R,S*)-**4a**, 56533-18-7; (*S*)-**4a**, 56586-19-7; (*R,S*)-**4b**, 56533-19-8; (*S*)-**4b**, 56586-20-0; (*S*)-**5**, 56533-20-1; (*R*)-2-phenylaziridine, 18142-08-0; phenyl isocyanate, 103-71-9; phenyl isothiocyanate, 103-72-0; (*R*)-2-amino-2-phenylethanol, 56613-80-0; (*R*)-1-(1′-phenyl-2′-hydroxyethyl)-3-phenylurea, 56533-21-2; (*R*)-1-(1′-phenyl-2′-hydroxyethyl-3-phenylthiourea, 56533-22-3; (*R,S*)-1-phenyl-2-aminoethanol, 1936-63-6; (*S*)-1-phenyl-2-aminoethanol, 56613-81-1; (*S*)-mandelic acid, 17199-29-0; *p*-toluenesulfonic acid, 104-15-4; $BF_3$·$OEt_2$, 109-63-7; *p*-nitrobenzoic acid, 62-23-7; picric acid, 88-89-1.

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